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Nitridation Behaviour of Silicon with Clay and Oxide Additions: Rate and Phase Development

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Abstract

Samples pressed from fine powders of Si, Si + SiO$_2$, Si + kaolinite and Si + SiO$_2$ + Al$_2$O$_3$ were nitrided by both the nitrogen demand method and a constant rate of heating using a graphite resistance furnace at temperatures of 1100 to 1450°C. The nitridation rate for different compositions and input parameters were determined by continuously monitoring the time, temperature and pressure within the furnace. By comparing the different compositions, the effect of impurities, silica and particle size on nitriding rate, phase composition and percent theoretical weight gain were determined. Compositions containing high purity additives were found to nitride at higher temperatures and to be more susceptible to weight loss during nitridation. The prime cause for low weight gains was determined to be volatilization of silicon out of the samples. Si$_2$N$_2$O/O' Sialon was formed in all compositions containing the as-used additives and acted to retain the oxygen within the sample. © 1997 Elsevier Science Limited.

1 Introduction

The nitridation of Si can be used to produce self-bonded silicon nitride, sialons and oxynitrides as porous refractory bodies and as materials to be sintered to dense structural components. To obtain specific phases and to improve processing and properties, compounds such as silica,[1] alumina,[2] aluminum,[3] aluminum nitride,[4,5] clays,[6] refractory oxides[2,5] and silicon carbide[6,7] can be added to the silicon prior to nitridation. The use of these additives often allows for increased rates of nitridation over that of pure silicon which is known to require a long time for successful nitridation due to the highly exothermic nature of the reactions between silicon and nitrogen.

Due to the difficulties in nitriding silicon, much emphasis has been placed on understanding the effects of impurities, particle size, and heating schedule on the kinetics of these reactions.[8,9] Impurities/additives have been shown to affect nitridation by both interacting with the silicon particle and the silica surface layer found on it. Specifically, iron has been shown to help initialize nitridation, either by reacting directly with the silicon to form iron silicides[10] or by causing devitrification and removal of the silica surface layer on the silicon particle.[11] The susceptibility of the silica layer to the effects of iron impurities in the early stages of nitridation have been related to the thickness of the silica layer.[12] The addition of sintering aids such as yttria have been shown by transmission electron microscopy (TEM) analysis to aid the early stages of nitridation by reacting with the silica surface layer and allowing more controlled removal of it.[13] CaO[14] and MgO[15] additions have been shown to enhance the overall rate of nitridation and allow for it to occur at lower temperatures.[16] Similarly, iron impurities have been shown to lower the temperature of nitridation.[11]

The presence of impurities and additives has also been demonstrated to affect the phase content of nitrided materials. Iron impurities have been reported to increase the β-Si$_3$N$_4$ content[11] while CaO and MgO additions/impurities increases the α-Si$_3$N$_4$ content.[14,15] Silicon oxynitride has been shown to form when silica is added to silicon,[1,17] while sialons, both α and β, can be formed when aluminum nitride[2,4,5] and/or alumina is added to the silicon.

In this paper, the effect of clay, silica and silica plus alumina on the rate of nitridation versus temperature, and the phases formed, will be presented. In particular the role of impurities and silica on the nitridation process will be investigated. During nitridation, silicon and silica should have the effect of oxidizing and reducing each other and determining this relationship in the presence

of impurities is important in understanding the reactions which take place, particularly those involving alumina and mullite. It is also a first step in understanding the nitridation behavior of mixes containing clays and other phases such as silicon carbide and aluminum. In general the use of clays in ceramic processing, particularly for refractories, is advantageous due to their inherent plasticity, low cost, abundance as a natural resource and their availability in a variety of purities and mineralogical forms. Clays are commonly added to Si and nitrided with coarse refractory grade SiC to produce nitride bonded SiC[5,6] where the bond phase can consist of beta sialon, silicon nitride and O' sialon. Understanding their effect on nitridation both in terms of purity and quantity is, therefore, of both technological and scientific interest.

2 Experimental

2.1 Powder compositions and processing

Tables 1 and 2 show the particle sizes and major impurities for the different Si powders used in this study. For preliminary runs in which silicon powder was the sole constituent of the mix, the fine, high purity 4D (Grade 4, Size D) powders were used. These samples were dry-pressed using as-received powders moistened with propanol, a steel die with a diameter of 30 mm and a pressure of 100 MPa. The pressed pieces had a thickness of 7–10 mm and a weight of 6–8 g.

Mixtures of $Si + SiO_2$, $Si + SiO_2 + Al_2O_3$ were mixed by roller mill in poleythlene containers for 1 h using methanol, SiAlON balls and a low powder to milling media ratio, 1 : 2, to facilitate mixing but avoid significant milling. Two different grades of silica were used, a coarse < 325 mesh high purity reagent grade silica (Johnson Mathey) and a fine-grained silica made from NH_3 stabilized colloidal silica (Eka Nobel, $30NH_3/220$) that had been comminuted after destabilization with propanol and drying. It had a specific surface area of $\approx 220 \, m^2 \, g^{-1}$. The alumina (Alcoa, A16SG) was a fine grained, 0·6 micron, and of high purity. The powders after drying were pressed in the same manner as the pure silicon samples.

Table 3 shows the chemical composition and particle sizes of the three different grades of kaolinite clay used in this study. They will be designated LP (lowest purity), MP (medium purity), and HP (highest purity) in this text. The MP clay contains 7 wt% montmorillonite. The powders of silicon + clay were mixed by roller mill in poleythlene

Table 1. Particle size distribution of Sicomill® Si powder from permascand

Size	Particle size distribution		
	d_5	d_{50}	d_{90}
B	5	25	50
C	2	7	12
D	1	5	9

Table 2. Major impurities in Sicomill® Si powder from permascand

Element	Weight %	
	Grade 2	Grade 4
Fe	0·40	0·07
Al	0·20	0·07
C	0·05	0·01
Ca	0·06	0·10
O	0·2–1·0	0·2–1·0

containers for 1 h using distilled di-ionized water and SiAlON balls. The solid to water ratio by weight was 1 : 1 and a low powder to milling media ratio, 1 : 2, was also used. The pH for the slurries were close to 7, an intermediate value between that of pure clay slurries, pH = 5, and of silicon, pH = 9. After drying the mixtures the powders were coarsely sieved and pressed in the same manner as powders made from silicon and silicon + oxides. Samples after pressing were dried at 115°C for 24 h.

To consider the effect of mixing the clay and silicon in water, a calcined clay (Glomax, Dry Branch Kaolin) with a similar chemical composition as the HP clay was mixed with silicon using propanol. The average particle size of the calcined clay was 1·3 μm which was slightly greater than the HP clay.

2.2 Nitridation furnace

The nitridation experiments were performed in a graphite furnace equipped with a vacuum system

Table 3. Chemical analysis and average particle size of clays

Manu. Grade	Dry Branch Kaolin Hydrite R	Amberger Kaolin. Eduard Kick OKA	ECC Intern. Grade D
SiO_2-	45·5	52·7	46·88
Al_2O_3-	38·5	34·0	37·65
Fe_2O_3-	0·3	0·4	0·88
TiO_2-	1·4	0·15	0·09
CaO-	0·05	0·15	0·03
MgO-	0·05	0·22	0·13
K_2O-	0·05	0·25	1·60
Na_2O-	0·1	0·05	0·21
LOI-	13·8	12·2	12·45
d_{50}	0·8 μm	1·3 μm	2·0 μm

and a computer interfaced gas flow pressure system that could be run using either the nitrogen demand method or a simpler constant rate of heating method. For the nitrogen demand method, the furnace is run by the principle that when the nitrogen consumption ($\Delta P/\Delta t$) exceeds a certain value, the furnace should stop heating and stay constant in temperature until the nitrogen consumption rate decreases to the selected value. As such, a heating rate, a fill pressure, a ΔP (fill pressure–lower pressure limit) and Δt (time between fills) are programmed. To perform constant rate of heating experiments, ΔP and Δt are chosen so as not to stop the heating.

2.3 Nitriding conditions

All samples were heated to a temperature of 1100°C in a low vacuum, 10^{-2}–10^{-3} atmospheres, before nitrogen was introduced. For samples containing clay, a two-stage heat treatment in vacuum was used, 250°C/h to 1050°C and 33°C/h to 1100°C while, for the non clay-containing samples, a single heat treatment was used, 250°C/h to 1100°C. At 1100°C, a mixture of 95 vol% N_2 and 5 vol% Ar was filled to a pressure of 900 mbar. This was the upper fill pressure and, for all fills during nitridation, only N_2 was added, thus keeping the Ar pressure near constant. The values for ΔP and Δt were selected according to experience and the desired purpose of the experiments. All samples were heated to a final temperature of 1420–1440°C unless otherwise noted. The control parameters were calculated in terms of rate of nitrogen consumption per gram of silicon, mbar $min^{-1} g^{-1}$. The control parameters were varied from value of 0·0025 mbar $min^{-1} g^{-1}$ for pure Si to a value of 0·025 mbar $min^{-1} g^{-1}$ for some of the clay-containing samples.

For calculation of the control parameter, the effect of temperature on pressure was neglected. This assumption has only a small effect on the control parameter for most compositions. For the silicon samples, however, which can experience sudden nitridation, the control parameter can be effectively increased by a factor of 1·5 by this effect. The pressure increase due to temperature over the range of 1100 to 1450°C was found to equal 30 mbar per 100°C or (0·3 · ΔT) mbars.

2.4 Calculation of weight gains and nitrogen consumption rate

The nitrogen pressure was recorded by computer every 20 to 60 s depending on the length of the run and the speed of the reaction. For calculating the nitrogen consumption rate, the time between fills, Δt, and the actual decrease in pressure between fills, equal to $\Delta P + 0\cdot3\Delta T$, was used. The nitrogen consumption rate per gram of silicon is therefore

$$= \frac{(\Delta P + 0\cdot3\Delta T_F)/(\Delta t)}{m}$$

where ΔT_F in this case is the temperature difference between fills and m the total mass of Si.

The weight gain due to nitridation was measured for all samples. The theoretical weight gain for a sample was calculated by assuming that only the silicon reacts with nitrogen and that it reacts only to Si_3N_4. Thus, the

$$\text{theor. wt gain} = \left(\frac{\text{Mol. Wt } Si_3N_4}{\text{Mol. Wt } 3\cdot Si}\right) \\ \times (\text{Wt\% Si})(\text{orig. wt}) - (\text{orig. wt})$$

and

$$\% \text{ theor. wt gain} = \frac{\text{actual wt gain}}{\text{theor. wt gain}}$$

For the clay-containing samples the loss on ignition (LOI) was subtracted from the theoretical weight gain. The theoretical weight was averaged for all samples and was found to vary generally by less than 5 %.

2.5 X-ray diffraction

To determine phase content after nitridation, X-ray diffraction (XRD) was performed on cross-sections of selected samples in each run. In addition, for certain runs which had experienced lower than expected weight gain, XRD was performed on the surface and near surface of the samples. Results will be presented for selected runs.

3 Results

3.1 Nitridation of Si

For the purpose of comparison with samples containing additives, Figs 1(a–c) show the rate of nitrogen consumption versus time and temperature for three sets of samples made from high purity silicon, 4D, run at different heating rates and control parameters. From these plots, it is seen that after an initial period of slow reaction there is a main reaction peak at 1225°C. For the samples heated at 2·5°C/h and 0·0025 mbar $min^{-1}g^{-1}$, and 3°C/h and 0·003 mbar $min^{-1} g^{-1}$ a second main reaction occurs at temperatures between 1350 and

1400°C while, for the samples heated at 7·5°C/h and 0·0075 mbar $min^{-1}g^{-1}$, no obvious second reaction occurs. The samples heated at 7·5°C/h contain large beads of silicon in the sample, indicating runaway nitridation had caused melting. For the samples heated at the slower rates, 2·5 and 3·0°C/h, the first reaction peak is more controlled and no significant difference in reaction rate is seen. The nature of the second reaction peak, however, appears to be extremely sensitive to reaction temperature. The run at 2·5°C/h shows a reaction that is very controlled over a wide temperature range and has a high theoretical weight gain, 83%, while the run at 3·0°C/h is similar to it

initially, but shows a rapid reaction at a temperature of ≈ 1400°C, which is close to the melting temperature of silicon, 1409°C. The theoretical weight gain for the samples heated at 3·0°C/h is only 68% and, unlike the samples heated at 7·5°C/h, shows no evidence of melted silicon either visually or in X-ray diffractograms. The samples heated at 2·5°C/h, however, did show traces of silicon in the X-ray diffractogram. This suggests that the fast reaction at 1400°C for the samples heated at 3·0°C/h resulted in volatilization of silicon out of the samples and low weight gain. The α/β ratio for the samples heated at 2·5 and 3·0°C/h is also much different, with the samples heated slowly having an α/β ratio of 2 and those heated faster a ratio of 0·5.

3.2 Nitridation of Si + SiO$_2$

Figure 2(a) shows the nitrogen consumption rate versus time and temperature for a set of samples containing 85 wt% 4D Si and 15 wt% SiO$_2$ (< 320 mesh) that were heated at a rate of 3°C/h and a control parameter of 0·003 mbar $min^{-1}g^{-1}$. It is seen that, like the pure silicon samples, there are two main reaction peaks. The reaction at low temperature, however, is more rapid in nature than
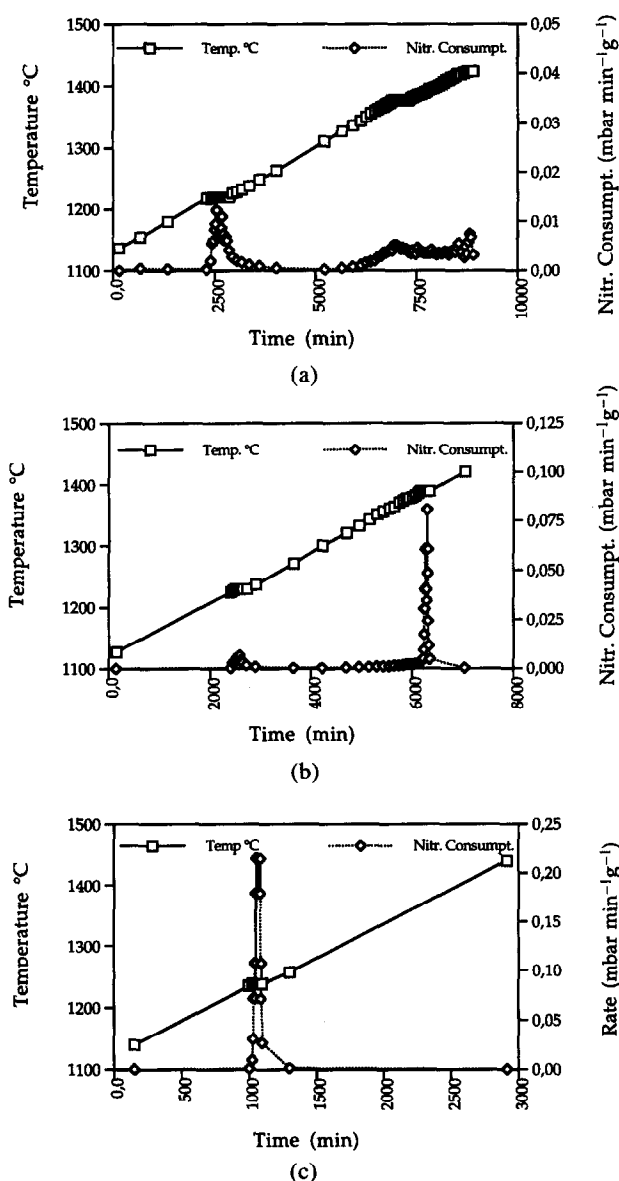

Fig. 1. Temperature and nitrogen consumption rate as a function of time for 4D silicon nitrided with (a) heating rate of 2·5°C/h and a control parameter of 0·0025, (b) heating rate of 3°C/h and a control parameter of 0·003 and (c) a heating rate of 7·5°C/h and a control parameter of 0·0075.
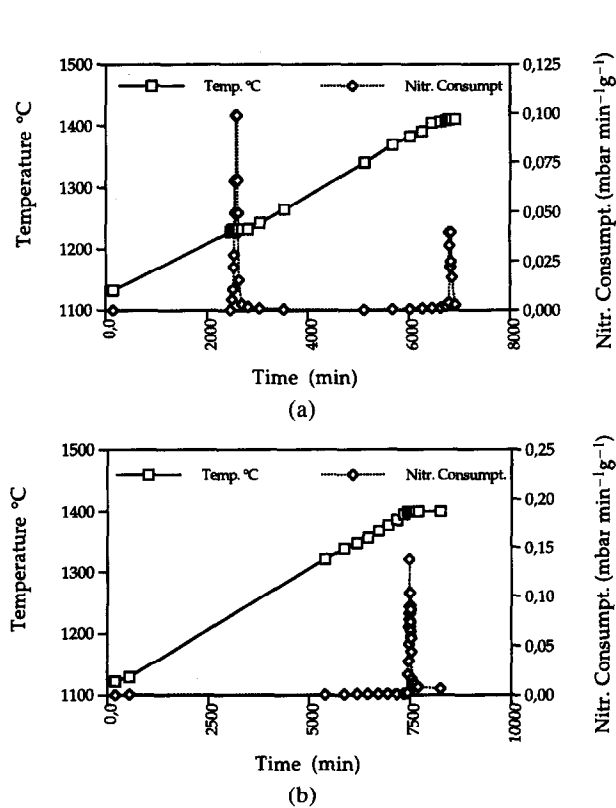

Fig. 2. Temperature and nitrogen rate as a function of time for composition of 85 wt% 4D silicon and 15 wt% silica with a heating rate of 3°C/h and a control parameter of 0·003. For (a) a coarse < 320 mesh silica was used and in (b) a fine submicron silica was used.

the run of pure silicon with the same reaction parameters. The theoretical weight gain for these samples is 68%. X-ray diffraction of these samples shows approximately equal amounts of α- and β-Si_3N_4 and substantial amounts of Si_2N_2O.

Figure 2(b) shows the nitrogen consumption rate versus time and temperature for samples of the same composition and reaction parameters as above but with a fine grain high purity silica as the additive. In this run, there is a lack of significant reaction until a temperature of 1375°C whereupon rapid nitridation occurs. The theoretical weight gain for these samples is extremely low at 29% and the phase composition for a cross-section of the sample consists primarily of a mixture of Si_2N_2O, β-Si_3N_4 and some α-Si_3N_4. The presence of Si_2N_2O and the lack of unreacted silicon in the interior of the sample suggests that the low weight gain is primarily caused by volatization of silicon out of the sample and not a loss of SiO vapor formed by the reaction between Si and SiO_2. The silica is needed to form Si_2N_2O. The surface of the sample, however, has a lower Si_2N_2O content, indicating some loss of SiO vapor from the sample.

3.3 Nitridation of Si with different oxide/clay additions

For the purpose of comparison, a run containing several different Si + LP clay and Si + SiO_2 + Al_2O_3 compositions was performed at a slow heating rate of 2·5°C/h, a control factor of 0·0025 mbar

Table 4. Compositions and reaction products for a material heated at 2·5°C h^{-1} and a control factor of 0·0025 mbar min^{-1} g^{-1}

Composition	% Theoretical Wt Gain	Phase Composition
80 Wt% Silicon (4D) 20 Wt% Kaolinite (LP)	82%	α-Si_3N_4 β-Si_3N_4 O'Sialon Mullite χ-Phase
60 Wt% Silicon (4D) 40 Wt% Kaolinite (LP)	93%	α-Si_3N_4 β-Si_3N_4 O' Sialon Mullite χ-Phase
63 Wt% Silicon (4D) 20 Wt% Silica (coarse) 17 Wt% Alumina	64%	O' Sialon β-Si_3N_4 β-Sialon Al_2O_3 α-Si_3N_4
63 Wt% Silicon (4D) 20 Wt% Silica (fine) 17 Wt% Alumina	34%	O' Sialon β-Sialon β-Si_3N_4 Al_2O_3 α-Si_3N_4

min^{-1} g^{-1} and a maximum temperature of 1450°C with a 5-h hold. Table 4 shows the percent theoretical weight gain and the phases formed after nitridation from the various compositions.

From this table, it is seen that samples made from Si + SiO_2 + Al_2O_3 mixtures showed a low percent theoretical weight gain, particularly the composition made from the fine-grained silica. As in the samples made from only silicon and silica, these compositions show substantial silicon oxynitride formation and no residual silicon. Besides silicon oxynitride, these samples contain β-Si_3N_4, β-SiAlON, residual alumina and minor amounts of α-Si_3N_4. The sample made with colloidal silica showed higher sialon contents and lower alumina contents. Figure 3 shows an x-ray diffractogram of this sample and it is seen that beta sialon is formed, but the broad nature of the peaks indicates that it has a range of z values and is not fully reacted. These samples, like those made with Si + SiO_2, has a reduced silicon oxynitride content on the surface.

The clay-containing samples show greater percent theoretical weight gains than the samples of the same nominal composition made with purity silica and alumina. The phase composition of the clay at the temperatures of nitridation is a mixture of silica and mullite/psuedo-mullite. The formation of mullite, a silica-containing phase, reduces the amount of free silica from that of the pure silica + alumina compositions. The wt% free silica for a sample with 40 wt% clay that has reacted to stoichmetrically pure mullite and silica is 9·6 wt% and would correspondingly have a silicon to free silica ratio of approximately 85 : 15. This is the same ratio as the two silicon + silica samples discussed earlier.

After nitridation the clay-silicon materials show a phase composition of Si_2N_2O, α-Si_3N_4, β-Si_3N_4, χ-phase and mullite. Unlike the alumina + silica samples, no beta sialon is formed, suggesting that the mullite remains unreacted.

3.4 Nitridation of Si + clays

Figure 4 shows the nitrogen consumption versus temperature for a mixture of 60 wt% 4D silicon and 40 wt% LP clay heated at 15°C/h to a temperature of 1400°C with no gas control parameter. From this plot, it is seen that nitridation commences at low temperatures but only at a temperature of $\approx$ 1275°C does a distinct reaction peak become discernible. The theoretical weight gain is 87% and the phase composition is α-Si_3N_4, Si_2N_2O, β-Si_3N_4, mullite and some residual Si. The presence of silicon probably indicates that the final temperature

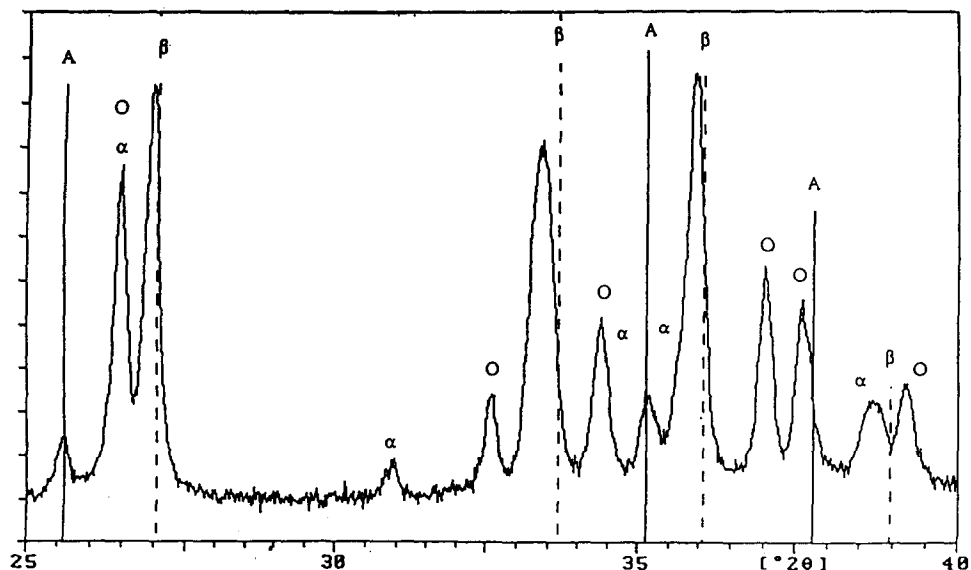**Fig. 3.** An x-ray diffractogram showing the diffraction peaks from 25 to 40 2θ for a nitrided sample of $Si + SiO_2 + Al_2O_3$. The reference lines are for alumina-A, and β-silicon nitride-β while O and α correspond to O' SiAlON and α-silicon nitride. The alumina peaks are seen to correspond in loacation to the reference line while β peaks are seen to be offset indicating SiAlON formation.

for nitridation was too low for full reaction while the lack of the χ-phase likely indicates that this phase formed at the higher reaction temperatures in the previous run. Besides these differences, the phase composition and weight gains of these materials are quite similar to the slow run despite the great differences in heating rate and control parameters used. An X-ray diffraction of this sample is shown in Fig. 5(a).

When the type of clay is changed to an HP variety, the nature of the reaction curves, the percent theoretical weight gain and the phases formed are affected. Figure 6 shows that the main nitridation peak occurs at a higher temperature and is more rapid while the theoretical weight gain, 40%, is quite low. From the X-ray diffraction, see Fig. 5(b), it is seen that, in comparison to the sample made with the lowest purity clay, the mullite content is substantially reduced and the beta silicon nitride peak is increased in relative intensity to the alpha

Fig. 4. Rate of nitrogen consumption as a function of temperature for samples containing 60 wt% 4D silicon and 40 wt% LP clay and heated at 15°C/h with no control parameter.

peak, and seems to be shifted to lower angles, indicating that some beta sialon has formed. In addition, the presence of silicon oxynitride/O' sialon is seen in this X-ray diffractogram. Silicon oxynitride and O' sialon form a limited solid solution that can result in small shifts in X-ray peaks.

The nitridation behavior for a 60:40 mixture of the 4D silicon and the MP clay is very similar to that of the HP clay except that the main reaction is slightly less violent and occurs at a slightly lower temperature, $\approx 5-10°C$. Some beta sialon is also evident in these materials. The main difference between the MP and the HP clays is a higher alkali content.

Figure 7 shows there is a significant decrease in the nitridation temperature when a low purity silicon with high iron contents is substituted for the high purity silicon in a mixture containing the high purity clay. In this run it is likely that some of the decrease in the rate of nitridation can be attributed to the use of the control parameter. But, by comparing the rate of nitridation at temperatures before the control parameter stops heating, it is clear that the use of the low purity silicon causes nitridation to occur at lower temperatures and in a more controlled manner. It can also be seen from the relatively small difference between the control parameter, $0.016\,\text{mbar}\,\text{min}^{-1}\,\text{g}^{-1}$, and the maximum rate of nitridation, $0.025\,\text{mbar}\,\text{min}^{-1}\,\text{g}^{-1}$, that the chosen control parameter is sufficient for controlling the reaction. The controlled reaction results in high weight gains, 88%, similar to that found for the lower purity clay. The phase composition is also similar to the samples made from the lower purity clay.
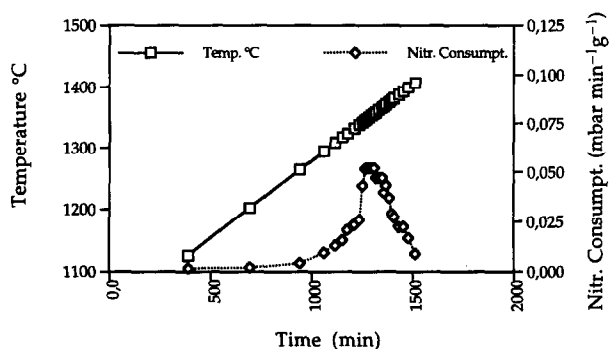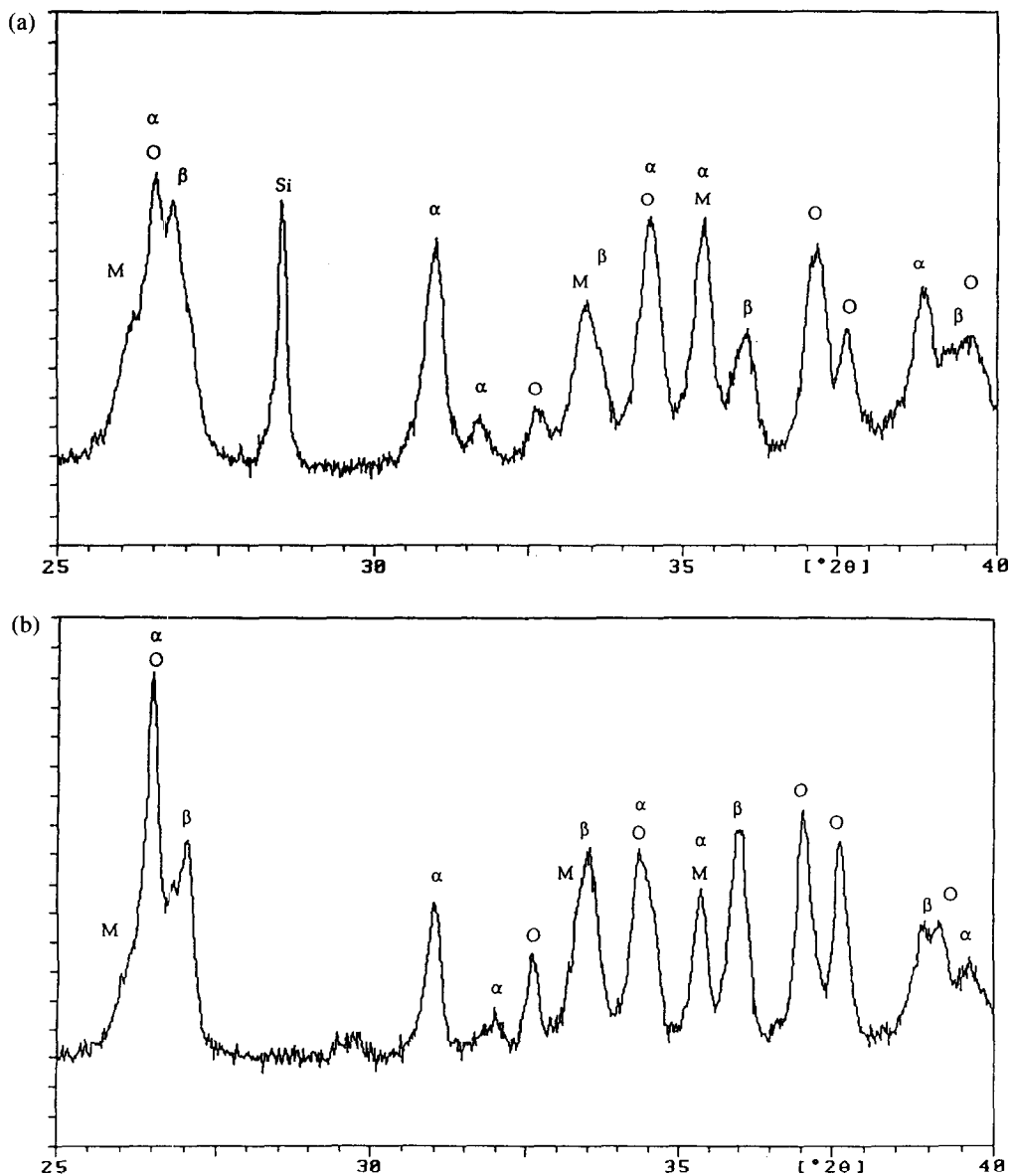
Fig. 5. An x-ray diffractogram showing the identified diffraction peaks from 25 to 40 2θ for (a) nitrided sample containing 60 wt% 4D silicon and 40 wt% LP clay and (b) containing 60 wt% 4D silicon and 40 wt% HP clay. α, β, M, O, and Si correspond to α-silicon nitride, β-silicon nitride, mullite, O' SiAlON and silicon.

To better understand possible effects clay has on nitridation, pressed samples of LP clay were heated to 1300°C without silicon or a powder bed. These samples, after heating, showed densification and were enveloped by a web of fine fuzz. This indicates that the clay is active at these temperatures in terms of sintering and that, when heated in a reducing atmosphere, the clay partially volatizes and is reactive with nitrogen. To consider the effect of processing the clay-silicon samples in water, a sample of a calcined clay with the same impurity content as the HP clay was mixed in propanol with Si and nitrided. These samples displayed similar nitridation behaviour as the run shown in Fig. 6, except that the nitridation commenced at slightly lower temperatures, ≈ 10°C.

3.5 Effects of reduced clay contents

Figure 8 shows the nitrogen consumption versus temperature and time for a mixture of 80 wt% percent 4D silicon and 20 wt percent of MP clay. For this run a heating rate of 15°C/h and a control parameter of 0·008°C/h were used. This run, like the run with HP clay shown in Fig. 6, and the 60:40 of the MP clay discussed earlier, showed little reaction at temperatures less than 1300°C, suggesting that the clay at these concentrations still has a strong effect. The reactions that peak at higher temperatures, however, seem to be more affected by the decrease in the amount of clay and instead of one single nitridation peak at a temperature of 1350–1370°C, two or three reaction peaks are apparent, with the final occurring at
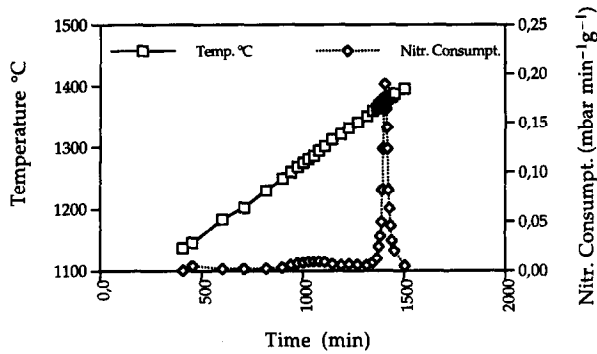
Fig. 6. Rate of nitrogen consumption as a function of temperature for samples containing 60 wt% 4D silicon and 40 wt% HP clay and heated at 15°C/h with no control parameter.

Fig. 8. Rate of nitrogen consumption as a function of temperature for samples containing 80 wt% 4D silicon and 20 wt% MP clay and heated at 15°C/h with a control parameter of 0·08 mbar mm^{-1} g^{-1}..

1400°C. The peaks at 1350–1370°C are similar in temperature to the main reaction peaks found for the 60:40 mixtures of silicon and MP/HP clays while the reaction at ≈ 1400°C is similar in temperature to that of pure silicon and silicon + silica samples.

Figure 9 shows the nitrogen consumption versus time and temperature for compositions of 80 wt% silicon 4D and 20 wt% LP clay heated at 15°C/h. In this run, a control parameter of 0·012 mbar min^{-1} g^{-1} was used and the reaction occurs primarily in two temperature ranges, ≈ 1275°C and 1400°C. The reaction peak at ≈ 1275°C is increased in initial rate over that of 60:40 composition made with this clay, shown in Fig. 4 but, like the other composition made with 20 wt% clay, it does not fully react until a temperature of ≈ 1400°C.

The weight gain for the two sets of samples made with 20 wt% clay is similar to that of the samples made with 40 wt% clay, 89% for the MP clay and 91% for the LP clay. The phase content for the two samples is also similar, with both having an α/β ratio close to 1, silicon oxynitride and traces of mullite. The silicon oxynitride content, as expected, is reduced from samples made with 40 wt% clay.
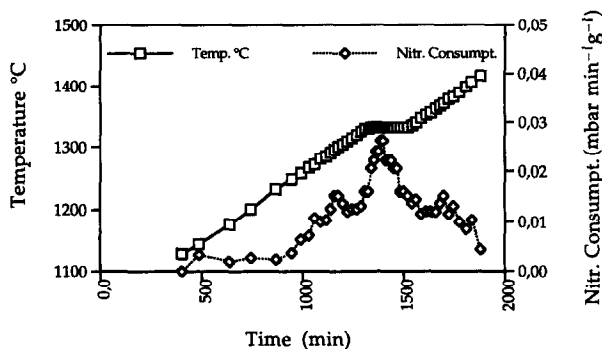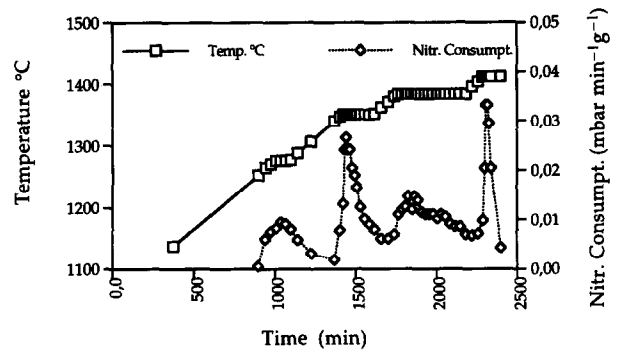
3.6 Effects of particle size and additives

The runs shown have all contained a fine-grained silicon, either grade 4D or 2D. Figure 10 shows the rate of nitrogen consumption versus time and temperature for a mixture of 60 wt% coarse silicon, 4B, and 40 wt% LP clay. Comparing this run to Fig. 4, it is seen that the nitridation starts at a similar temperature but the main reaction at ≈ 1340°C is less rapid and the theoretical weight gain is reduced to 84%. Results from X-ray diffraction indicate some residual silicon. Figure 11 shows the nitrogen consumption versus time and temperature for a mixture of 20 wt% 4B, 4C and 4D silicon mixed with 40 wt% of the HP clay heated at 7·5°C and a control parameter of 0·008 mbar min^{-1}g^{-1}. This sample shows a very controlled nitridation with a maximum rate of only 0·012 mbar min^{-1} g^{-1} and a fairly high theoretical weight gain of 82%. The sample, however, contains some residual Si. The phase composition consists of α-Si$_3$N$_4$, β-Si$_3$N$_4$, Si$_2$N$_2$O and mullite. Figure 12 shows the nitrogen consumption versus time and temperature for the same mixture as Fig. 11 but with 2 wt% yttria added and run at 15°C/h with no control parameter. For this run,
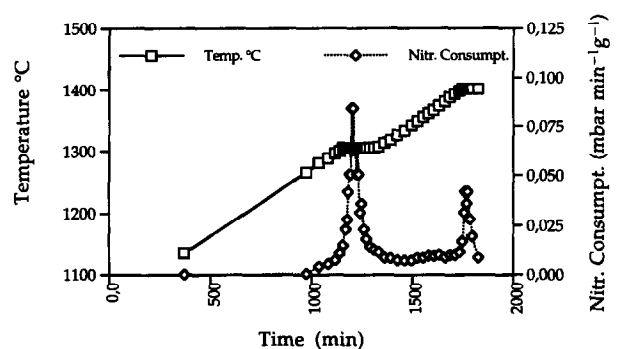

Fig. 7. Rate of nitrogen consumption as a function of temperature for samples containing 60 wt% 2D silicon and 40 wt% HP clay and heated at 15°/h with a control parameter of 0·016 mbar mm^{-1} g^{-1}.

Fig. 9. Rate of nitrogen consumption as a function of temperature for samples containing 80 wt% 4D silicon and 20 wt% LP clay and heated at 15°C/h with a control parameter of 0·012 mbar mm^{-1} g^{-1}.
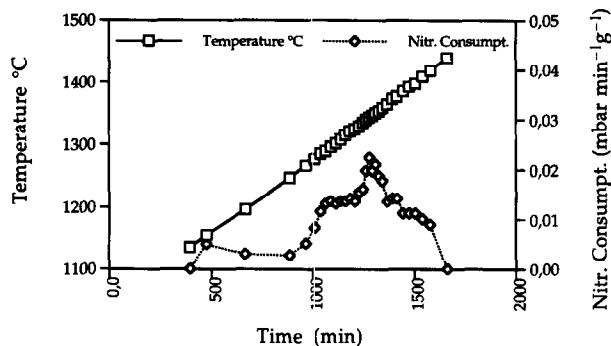
Fig. 10. Rate of nitrogen consumption as a function of temperature for samples containing 60 wt% 4B silicon and 40 wt% LP clay and heated at 15°C/h with no control parameter.

Fig. 12. Rate of nitrogen consumption as a function of temperature for samples containing 20 wt% 4B, 4C and 4D silicon, 40 wt% HP clay and 2 wt% excess yttria. Samples were heated at 15°C/h with no control parameter.

there is rapid nitridation at 1330°C with a maximum rate of $0 \cdot 10$ mbar min^{-1} g^{-1}. It shows a theoretical weight gain of 82% and there is no detectable silicon, suggesting that the decreased weight gain is due to volatization of material out of the sample. This material consists of β-Si$_3$N$_4$, Si$_2$N$_2$O, α-Si$_3$N$_4$ and mullite with possible traces of β-sialon.

4 Discussion of results

The initiation of rapid nitridation for silicon has generally been attributed to the removal of the oxide layer on the silicon particles.[10-13] From the experimental results, it is seen that both the temperature and rate of initial nitridation, and its sensitivity to heating rate, varies greatly with composition and particle size. Figures 2(a) and (b) showed that, for compositions containing 85 wt% fine silicon and 15 wt% silica, a coarse silica did not hinder initial nitridation at a temperature of $\approx$ 1225°C while a fine silica did. This difference in nitridation behavior at low temperatures is likely due to the differences in the chemical activity of the
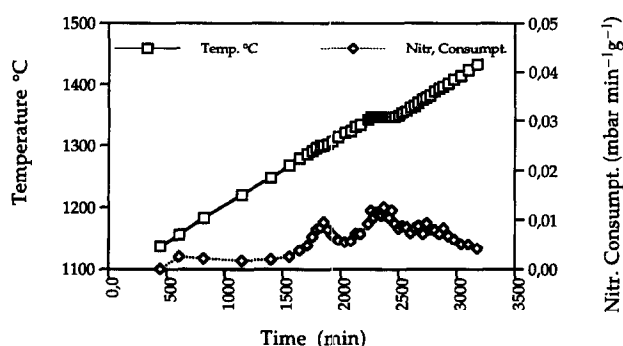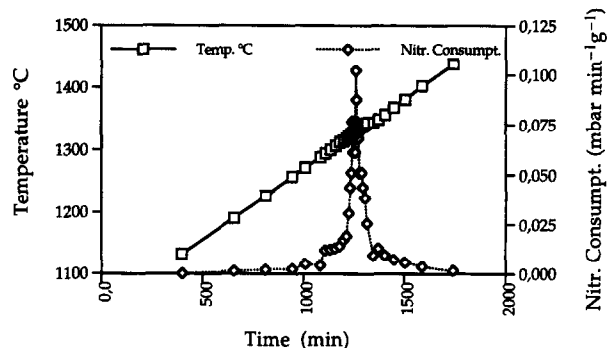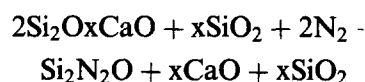

Fig. 11. Rate of nitrogen consumption as a function of temperature for samples containing 20 wt% 4B, 4C and 4D silicon and 40 wt% HP clay. Samples were heated at 7·5°C/h with a control parameter of $0 \cdot 008$ mbar min^{-1} g^{-1}.

fine and coarse silica and how well it disperses between the silicon particles. A fine grain silica is more likely to chemically react with the silicon particles, the silica on the silicon particles and the atmosphere than a coarse silica. Since fine grain silica is known to sinter at the temperatures of initial nitridation it is possible that it could sinter to the silica layer on the silicon particle and act to build it up. This would slow its removal from the silicon particle and result in slower nitridation rates. The presence of high surface area silica would also raise both the SiO and O$_2$ partial pressures in the compact and would therefore probably reduce both the rate in which the silica could volatilize and the rate of nitridation. A fine, in contrast to a coarse, silica would also separate the silicon particles from each other and prevent the rapid build up of heat that likely catalyzes nitridation in its initial stages.

The clay, like the colloidal silica used in Fig. 2(b) is fine-grained and has a relatively high surface area. It reacts at the temperatures of nitridation to a mixture of silica and mullite/psuedo-mullite[18] and, therefore, has many of the same physical and chemical properties as pure silica. The clay, however, contains more impurities than the silica and they can be expected to affect the nitridation behavior. Additives such as CaO have been added to pure silica + silicon compositions to help form silicon oxynitride ceramics by providing a liquid phase that oxidizes the silicon and is simultaneously reduced by it. The following reactions have been proposed for silicon oxynitride formation:[1]

$$3Si + (1 + x)SiO_2 + xCaO \rightarrow 2Si_2OxCaO + xSiO_2$$

$$2Si_2OxCaO + xSiO_2 + 2N_2 -$$
$$Si_2N_2O + xCaO + xSiO_2$$

CaO is a common constituent of clay and it and other alkalie/alkaline earths likely react in a similar manner with the SiO_2 and Si. The presence of alumina in clays, in the form of mullite, could lower the melt temperature from that of a pure silica-calcia melt. The mullite from the XRD results, however, is found to be most stable for compositions having the lowest purity clays. This suggests only a limited reaction between the mullite and the glass. Instead, the mullite appears to react the most in compositions with the highest purity. These compositions have the highest reaction temperature.

Another factor known to be of importance in determining the nitridation temperature is the iron content. Iron oxide is an impurity in all of the clays used and unlike the alkali and alkaline earth impurities which are likely incorporated into the glass as an oxide, the iron oxide could be either reduced directly to elemental iron depending on pO_2 pressure or incorporated into the glass. If the iron oxide is incorporated into the glass it would likely behave in the same way as the CaO except it could be possibly reduced to iron in the melt. Its effect on nitridation would likely be greater if it is reduced since it is known that iron silicides aid in nitridation.[8] Titanium oxide, a major impurity for pure hydrite clays, is probably unimportant since mixtures of TiO_2 and silicon are known to react to titanium nitride and silicon oxynitride.[19] The titanium would thus neither remain as an oxide capable of continuously forming glass like CaO nor react with Si to form a molten silicide like iron.

Figure 4 and Figs 6–12 showed the nitridation curves of different clay-containing samples. From them it is apparent that, as in the run containing fine-grain silica, the reaction peak at a temperature of $\approx 1225°C$ disappears. It is also apparent that samples made with the various clays behave in different ways. By comparing the results of the runs with the HP clay and those with the MP clay, it is seen that small increases in alkali and alkaline earth contents of the clays have only a small effect on the temperature of nitridation. It is also seen that the main temperature of nitridation for these compositions is just slightly reduced from that of the run with pure silicon + fine-grain silica.

For runs with the LP clay, which has both higher iron and alkalie/alkaline earth contents than the MP and HP clays, the temperature of nitridation is decreased considerably. The presence of both these types of impurities in the LP clay prevents the determination of their individual effects. But when an impure silicon with similar iron contents as the LP clay is added to the HP clay, the temperature of main nitridation becomes similar to that of the high purity silicon and LP clay (compare Fig. 4 and Fig. 7). This suggests that the iron content is of most importance in determining the nitridation behavior. It is, however, also seen that when a glass former like yttria is added to that of the HP clay (see Fig. 12), the nitridation temperature is lowered to a value close to that of the eutectic temperature of 1335°C for yttria-alumina-silica.[20] This shows the potential importance of localized melts and suggests the alkalie and alkaline earths probably cause some of the low temperature nitridation seen in Fig. 4.

From the above discussion, the importance of impurities in lowering the nitridation temperature is evident. It also is apparent from the results that samples containing higher concentrations of impurities show more controlled nitridation and higher percent theoretical weight gains. This phenomenon is likely due more to the temperature of nitridation than the actual impurity content. Nitridation is an exothermic reaction that can catalyze itself and result in 'run-away' nitridation. Samples that nitride at higher temperatures are therefore naturally more prone to this. As noted earlier in the results, the low weight gain in the HP clay- and oxide-containing samples seem to be due to volatization of material out of sample and not unreacted material since residual silicon is generally not present. The rapid reaction leading to volatization can be controlled somewhat in the HP clay-containing samples by increasing the average particle size of the silicon and reducing the heating rate (see Fig. 11). The very low weight gain for the samples containing silicon + silica + alumina heated at $2.5°C/h$, however, suggests this volatization can not be controlled solely by the rate of heating. Samples of pure silicon of the same particle size nitride extremely well at this heating rate and control parameters. Instead, it seems to be a result of the chemical reaction between the silicon and the additives.

Since silicon dioxide is not stable in a reducing atmosphere and the reaction between silicon and silicon dioxide is known to result in a high SiO vapor pressure,[8] it would seem possible that this reaction could be the cause of weight loss. The presence of significant silicon oxynitride however contradicts this conclusion because it requires the oxygen from the silica. Instead, only a significant loss of silicon as a vapor specie can explain these large weight losses. This can be illustrated by considering that, for a mixture of 85 g of Si and 15 g of SiO_2, the maximum possible weight gain is 56.7 g.

This assumes that all of the silica remains in the material as glass or silicon oxynitride. If, however, the silica reacts with silicon to form SiO gas that is lost by volatization, the total weight gain is reduced to 30 g or 53% of the theoretical. This calculated percent theoretical weight gain is greater than the 29% theoretical weight gain found for the sample made from 85 wt% Si and 15 wt% fine silica. Thus, the weight loss cannot be due only to silicon monoxide but has to be partially due to the loss of silicon vapor. Since silicon vapor is known to be highly reactive with nitrogen, it suggests that there is a depletion of nitrogen within the sample and that the nitridation rate of 0·15–0·20 mbar min^{-1} g^{-1} observed in Figs 1(c), 2(b) and 6 represents a maximum possible rate of nitridation for the samples tested and the furnace used. It should be noted that the run shown in Fig. 1(b) contained only silicon and similarly showed low weight gains without residual silicon.

The above observation of the silica being retained in the sample as silicon oxynitride suggests that the role of silica in causing excessive weight loss is indirect. Its effect can be considered by comparing the samples with 20 and 40 wt% clay. The samples with 20 wt% clay show more reaction peaks and require nitridation at higher temperatures for full reaction than samples with 40 wt% clay. The temperature of the final reaction nearly corresponds to that found for samples of pure silicon and suggests that the silica in the 20 wt% samples becomes depleted as a reactant. The samples containing 40 wt% clay contain both silicon nitride and silicon oxynitride, indicating that several reactions occur during the main nitridation peak. It thus seems likely that the heat from the reaction of SiO$_2$–Si–N$_2$ is quite high and catalyzes the reaction, forming Si$_3$N$_4$. Another possible explanation of Si$_3$N$_4$ forming at this temperature is that it forms from SiO vapor and the presence of increased silica increases this pressure. However, it has been noted in the literature that the reaction of SiO vapor to Si$_3$N$_4$ requires extremely low pO$_2$ pressures.[8] A low pO$_2$ pressure would seem unlikely in these compositions due to the high silica content. The similarity in the temperature for the other peaks found in the 20 and 40 wt% for all samples shows that the decrease in total impurity content for 20 wt% samples is unimportant in determining the reaction temperatures. Instead, the local impurity content in the clay seems to determine when the clay reacts during the nitridation process.

The above discussion of silica as a reactant is somewhat contradictory to the earlier discussion of how the silica slows the reaction by affecting the removal of the oxide surface layer on the silicon particle. The rate of this removal it was noted, determines how fast and, therefore, also how much heat is generated from initial nitridation of the silicon particle. This dual role of the silica likely explains why the reactions can be so different when the particle size or purity of the silica is changed.

In the clay-containing samples, the impurity content determines when the fine-grain silica reacts with the silicon and nitrogen. A consequence of this dependence is that the purer samples experience the highest temperatures during nitridation. This likely explains why the mullite, which is a high temperature phase with an eutectic temperature with silica of 1587°C, reacts to form beta sialon in the purest samples but remains a stable phase for samples containing LP clay. Whether the mullite is reduced or melted in these samples is difficult to speculate on from these results. However, it is clear that the nitridation process enables lower temperature formation of beta sialon compared to conventional means. The compositions tested generally require a temperature of 1600 to 1750°C to reach their equilibrium composition of beta sialon/ O′ sialon.

5 Conclusions

The results indicated that silicon samples containing 20 to 40 wt% of clay could be nitrided to high densities at fast heating rates of 15°C/h and that the need for restrictive control parameters increased with the purity of the clay and the amount of silicon. In addition, fine-grain silicon resulted in faster reactions and the increased probability of volatization. Samples containing high purity oxide additives were found to show a tendency to volatize despite slow heating rates.

From X-ray diffraction results and analysis of weight gains, it was concluded that silicon was the specie that was volatized in samples containing high purity additives and the oxygen from the clay/ silica was largely retained in sample as silicon oxynitride. Silica was found to initially hinder nitridation and prevent significant reaction at low temperatures but was found to be an active reactant at higher temperatures and, if present in sufficient quantities as fine additive, 15 wt% silica or 40 wt% kaolinite, result in a single reaction peak. The temperature of reaction depended greatly on the

impurities present with both iron and alkali/alkaline earths shown to decrease reaction temperature. Beta sialon formation was found to occur in samples that had the highest reaction temperature, between 1380 and 1410°C. These samples were characterized by only partial reaction to beta sialon. These results, however, illustrate the importance of silica and its quantity in determining the reactions taking place.

Acknowledgements

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